CO Monolayers on Pt(111) under Realistic Pressure

Scientific Achievement

Interaction of CO with Pt surfaces has been the model system for fundamental surface science for decades. The interest has recently been renewed due to CO poisoning in fuel cell cathodes. We have studied CO monolayers absorbed on Pt(111) surface at CO pressures directly relevant to the catalytic environment. We find that CO forms dense self-repairing self-protecting monolayers persistently poisoning and resilient to oxidation even when the layers appear no longer specifically chemisorbed. The dense layers exhibit fascinating two-dimensional behavior unexpected from chemisorbed systems.

At 1 atm, the CO layer forms (2x2)-3CO hexagon structure and at ~0.5 atm or lower pressure, it forms a larger commensurate ($\sqrt{19}\times\sqrt{19}$)-13CO pinwheel structure. These structures can reversibly transform from one to the other without coexistence regions. At an elevated temperature near ~100 ºC, relevant to the electro-catalyst operating temperature, these dense monolayers still maintain their respective dense layers but transform incommensurate structures. Interestingly, the hexagon structure transforms via a second-order phase transition while the pinwheel structure does via a first-order phase transition with a coexistence region. Detailed structure models were proposed based on surface x-ray scattering studies of the CO layer and the reconstruction of the underlying Pt layers. The structure models indicate strong interactions between CO and the substrate atoms as we would typically expect from chemisorption systems. Our observation of the incommensurate floating structures demonstrates that the collective, condensed-matter effects are important even for chemisorbed systems.

Significance

We found that CO forms self-repairing, self-protecting solid layers that are resistant to oxidation. Even though CO transforms from commensurate structures to an incommensurate floating layer at 300-400K, it remains a dense layer resistant to oxidation. The discovery of these incommensurate phases, typically seen before for physisorbed floating solids, challenges our understanding of chemical bonding between CO and Pt that is key to fully understanding the CO poisoning problem [A. Menzel, K.C. Chang, V. Komanicky, and H. You, submitted to Phys. Rev, 2006].

Performers

A. Menzel, K.C. Chang, V. Komanicky, and H. You (ANL-MSD)

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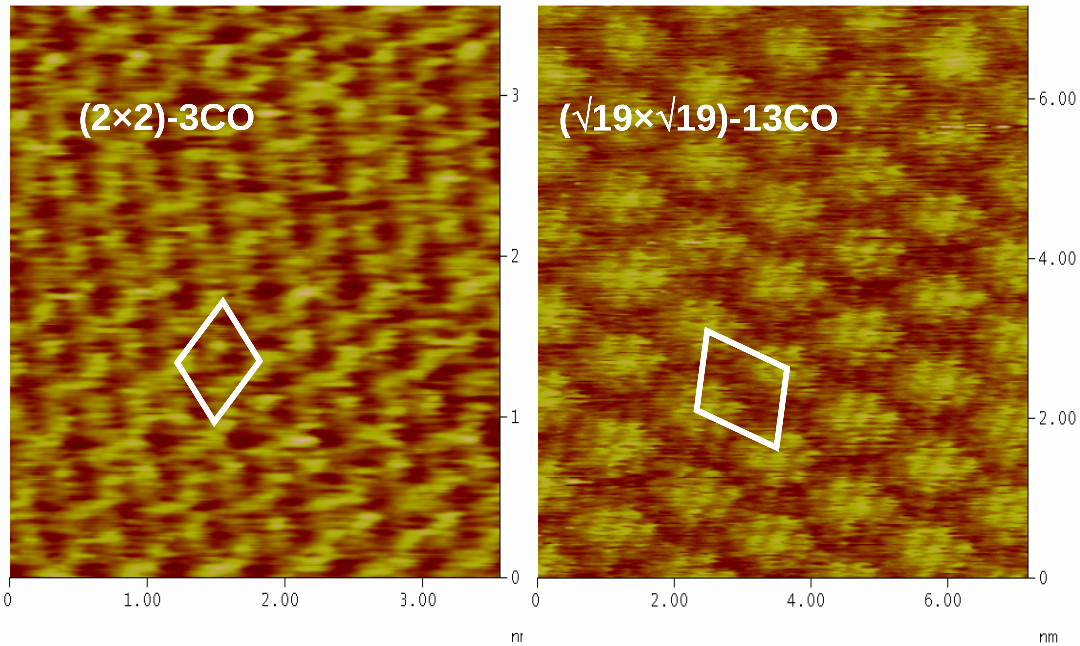

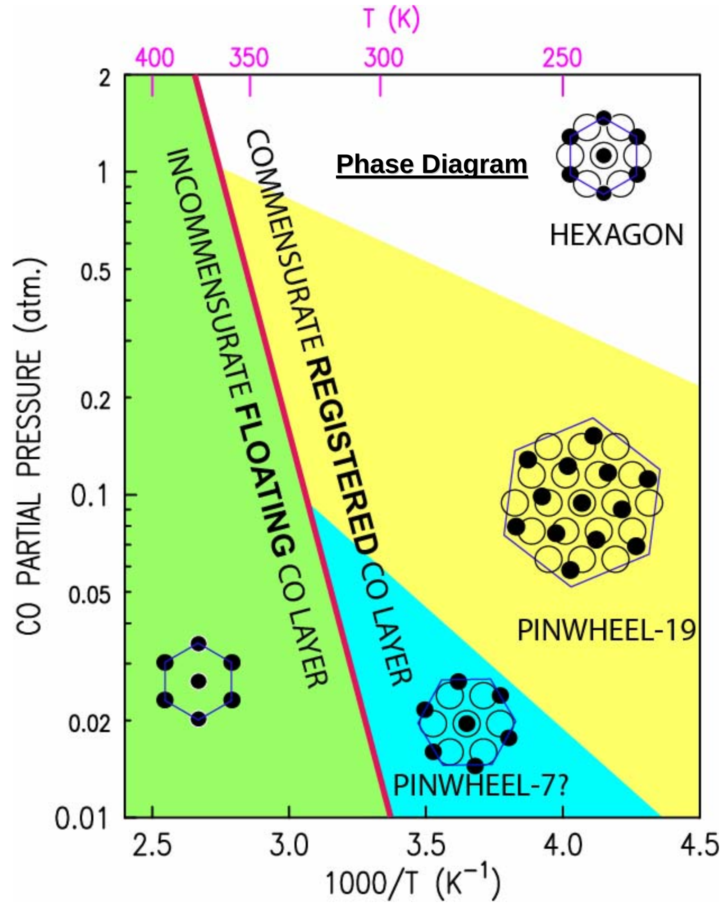

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ANL-MSD authors

A. Menzel, K.C. Chang, V. Komanicky, and H. You

Materials Science Division
ARGONNE NATIONAL LABORATORY

other authors (if any)